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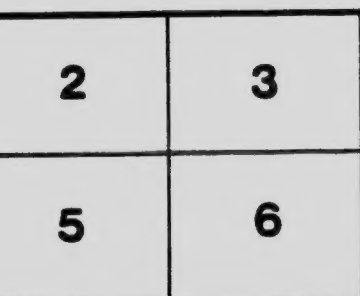
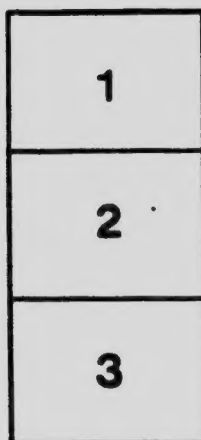
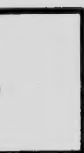
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STUDIES

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No. 70: COMPOSITION OF THE VAPOUR AND LIQUID
PHASES OF THE SYSTEM METHANE-NITROGEN, BY H. A.
McTAGGART AND E. EDWARDS

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*Composition of the Vapour and Liquid phases of the System
Methane-Nitrogen¹*

By CAPTAIN H. A. McTAGGART and MR. E. EDWARDS, M.A., B.Sc.

Presented by PROFESSOR J. C. McLENNAN, F.R.S.

(Read May Meeting, 1919.)

SYNOPSIS

1. Introduction. 2. Measurement of Temperature. 3. Gases Used. 4. Method of Analysis. 5. General Description of Apparatus. 6. The Cryostat. 7. Manipulation. 8. Results. 9. Summary.

INTRODUCTION

The problem—now a commercial one—of the separation of helium from natural gases bears a resemblance to the recovery of argon from the atmosphere. Helium occurs in the richest natural gas wells in about the same proportion—0.9%—as argon does in the atmosphere, and its separation at present is being effected in a similar way, *viz.*: by the method of liquefaction and rectification.

There is this difference, however, that while argon is recovered as a by-product in a very important industry, *viz.*: the manufacture of oxygen and nitrogen from the air, the separation of helium from natural gases is being carried out for its own sake. This adds considerably to the cost of production, a cost which might be reduced and probably will be when the liquefaction method as applied to natural gases is made more efficient.

A detailed examination of the conditions under which these gases liquefy ought to give useful information in this direction.

Wells yielding helium to any extent are found to contain as the chief constituents, methane and nitrogen. For example, a well in Texas, U.S.A., yields a gas of the following composition:

N, 34.0%; CH₄, 52.0%; Hydrocarbons, 12.3%; CO₂, 0.8%; O₂, 0.8%; He, 0.9%.

Another well in Alberta, Canada, has:

N, 8.1%; CH₄, 41.1%; CO₂, 0.1%; O₂, 0.1%; He., 0.5%.

For the present study the system CH₄-N was chosen for preliminary study, and the boiling points at atmospheric pressure of various

¹ Communicated by Professor J. C. McLennan, F.R.S., by permission of the Admiralty.

mixtures with the composition of the vapour and liquid phases are now given in this paper.

MEASUREMENT OF TEMPERATURE

Temperatures were measured by means of a Cu-Const. thermocouple, the E.M.F. being read on a slide wire potentiometer. An accumulator was used as a source of electric supply and a Weston cell as a standard.

The fixed points chosen for calibration were¹:

Boiling point of Nitrogen 77.3 abs.

" " " Oxygen 90.0 "

" " " Methane 109.0 "

at atmospheric pressure. The reference junction of the thermocouple was kept in melting ice.

Variations in the E.M.F. of the accumulator were corrected by frequent comparison with the Weston standard.

GASES USED

The Methane, oxygen and nitrogen used were all obtained commercially.

METHANE

This was obtained from Messrs. Insoles, Cymmer Collieries, Porth, Wales, and had a purity of 95% to 97%. The impurities, carbon dioxide, oxygen, nitrogen and hydrogen were removed by absorption and liquefaction followed by fractional distillation.

NITROGEN

This was supplied by the British Oxygen Company from their Birmingham Works, and was fairly pure. Any carbon dioxide present was absorbed in potassium hydroxide solution and the remainder liquefied. It was found to boil away at a fairly constant temperature.

These gases were stored separately in aspirator bottles over boiled water containing caustic soda in solution. These bottles were graduated roughly in half-litres. When a mixture was to be made, the two gases were admitted to the cryostat in the proportions desired, approximately, and liquefied.

This mixture, after a reading of it was taken, was stored in a third bottle and reserved for making other mixtures.

No attempt was made to prepare mixtures of a known composition but merely to obtain mixtures in sufficient variety for the purpose.

¹ Kaye and Laby's, Phys. and Chem. Constants.

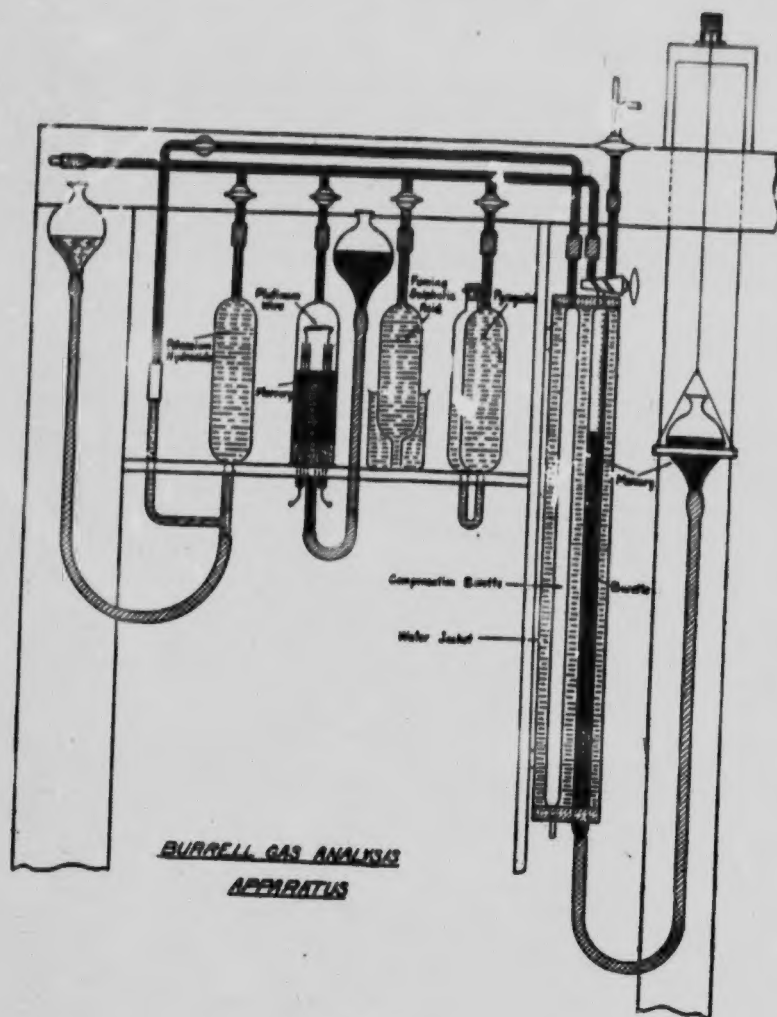
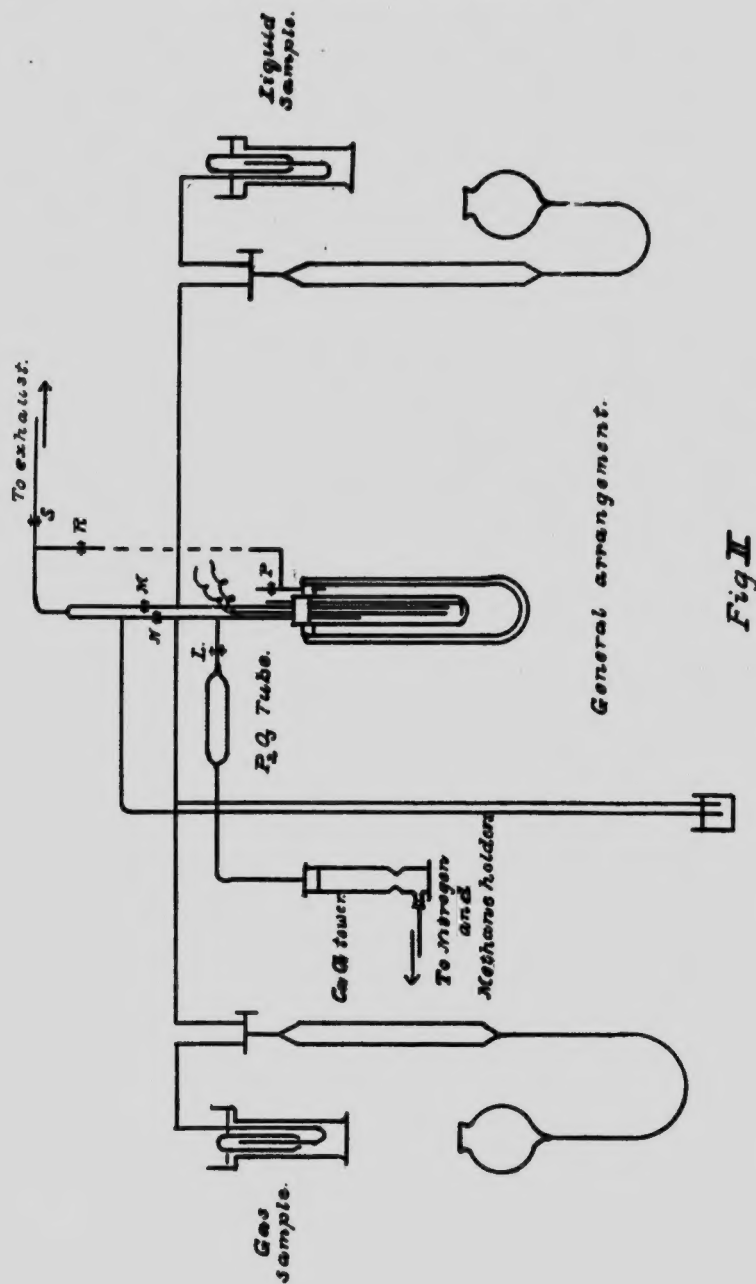


Fig. 1.

OXYGEN

This was used in calibrating the thermocouple and was obtained in the liquid form from the British Oxygen Company. A sample was allowed to boil away till the temperature became constant, any small percentage of nitrogen present in it boiling off in the process.



ANALYSES

The composition of any sample of methane-nitrogen was determined by estimating the methane by combustion and the nitrogen by difference. The apparatus used was of the Burrell Gas analysis type. A sketch is here attached, Fig. 1, showing the combustion chamber, KOH absorption pipette and the measuring burette. This latter could be read to hundredths of a cc.

GENERAL DESCRIPTION OF APPARATUS

Fig. 2 shows in diagram the essential features. The mixtures of methane and nitrogen were liquefied in a tube surrounded by a bath of liquid oxygen. This part of the apparatus is shown in the centre of the diagram and may be referred to as the cryostat. The mixtures were admitted to it after passing through drying tubes of calcium chloride and phosphorus pentoxide. Samples of the liquid and vapour phases were drawn off over mercury in burettes shown on each side of the diagram and collected in small sample tubes for analysis. In place of glass taps it was found convenient at some points in the apparatus to insert short lengths of rubber compression tubing which could be closed by screw clips. These are shown at L, M, N, P, R, S.

THE CRYOSTAT

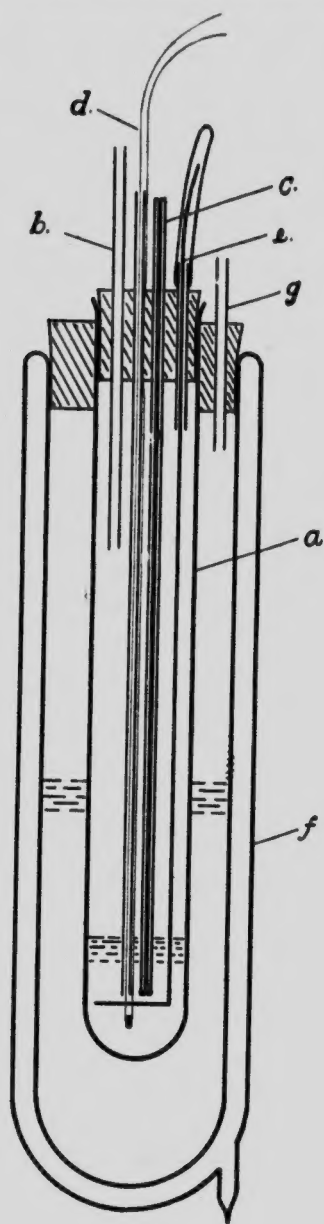
This is shown in detail in Fig. 3. The liquefying tube (*a*) was closed by a rubber stopper through which four small tubes passed, (*b*) used as exhaust tube as well as for the admission or withdrawal of gas samples, (*c*) a capillary tube used to withdraw samples of the liquid phase (this device was used by Baly, *Phil. Mag.* 49, 517, 1900), (*d*) a tube for the thermocouple wires—one wire running down inside it, the other outside—(*e*) a tube closed outside by a short length of rubber tubing and containing a glass stirring rod, which could be moved by hand through the rubber.

The vacuum flask holding the bath of liquid oxygen had part of the silvering removed so that the progress of liquefaction could be seen.

The flask was closed by a rubber stopper and connected by the tube (*g*) to an exhaust pump. By reducing the pressure to 5 cms. of mercury a temperature of -200°C . or lower could easily be reached. The pressures in the liquefying tube and in the vacuum flask were observed on simple mercury manometer columns.

MANIPULATION

In carrying out an experiment with any mixture the following order of proceeding was adopted. The liquefying tube was first exhausted through (*b*), the vacuum flask being removed. The storage

*Fig. III*

bottle containing the mixture was then connected to (b) and the vacuum flask with the bath of liquid oxygen placed in position. The temperature of the bath was then lowered if necessary by exhausting through (g). The liquefaction of any mixture took place quite readily when the temperature of the bath was kept about 5°C. below the boiling point of the mixture. When 7 or 8 litres had liquefied the flow was stopped and the vapour pressure allowed to rise to 1 atmosphere. This was done by raising the temperature of the bath or, in some cases, by lowering the bath. While the vapour pressure was kept at 1 atmosphere samples of both phases were taken, the first portion drawn off being rejected in each case. The liquid was kept thoroughly stirred to avoid any superheating and to ensure as complete an equilibrium as possible between the two phases.

RESULTS

The experimental results are given in Table I.

TABLE I

Temp. (abs.)	% CH ₄ in liquid phase	% CH ₄ in vapour phase
84.5	33.2	14.8
88.0	49.0	24.6
95.5	72.2	43.4
98.0	82.2	49.3
100.5	80.9	59.4
104.5	92.9	67.3
106.5	94.9	87.1

These numbers are shown graphically in Fig. 4 which constitutes a temperature-composition diagram.

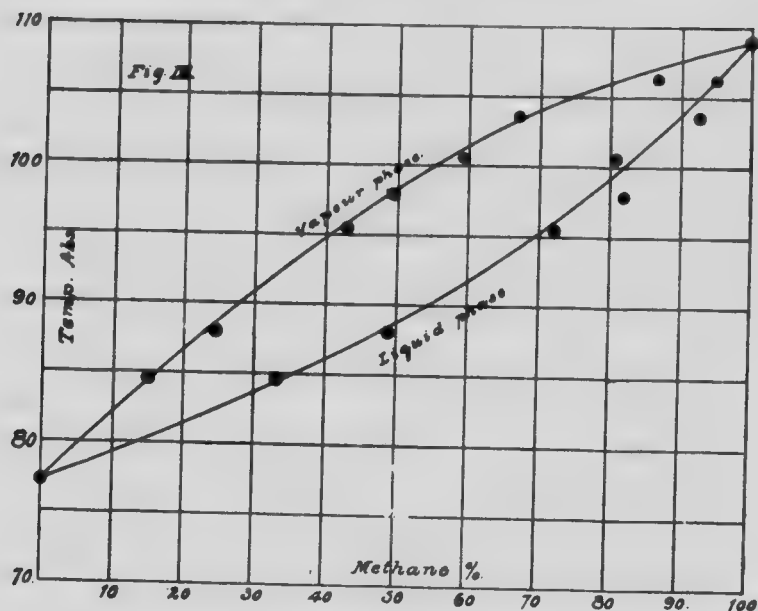
In Fig. 5 the composition of the liquid phase is plotted against that of the vapour phase, a few additional observations being added for which temperatures were not determined.

From this curve the relation:

$$\log r' = a + b \log r$$

where

$$r = \text{the ratio, } \frac{\% \text{ Methane}}{\% \text{ Nitrogen}} \text{ in liquid}$$



$$r' = \text{the ratio, } \frac{\% \text{ Methane}}{\% \text{ Nitrogen}} \text{ in vapour}$$

was found to hold very approximately, the constants in this case being:

$$a = -0.47$$

$$b = +0.85$$

as obtained from the graph.

This relation was used to obtain a more complete and smoother series of results. The corresponding temperatures were taken from the temperature composition diagram. Such a series (proceeding by two-degree intervals) is given in Table II.

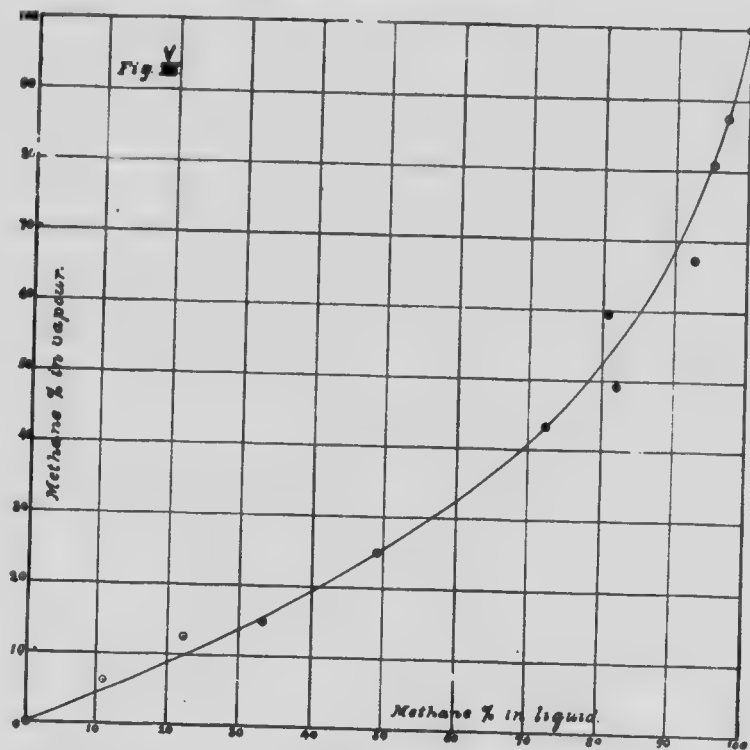


TABLE II

Temp. (abq.)	% Methane in liquid	% Methane in vapour
109°	100	100
108	98.4	92.0
106	94.8	80.0
104	90.5	69.6
102	86.0	61.6
100	81.6	54.5
98	77.0	48.7
96	72.4	43.5
94	66.6	37.6
92	61.0	33.0
90	54.2	28.0
88	47.0	23.3
86	39.4	19.0
84	30.6	14.4
82	22.2	10.0
80	13.0	6.0
78	3.4	1.5
77.3	0.	0.

SUMMARY

The temperature-composition diagram for the system methane-nitrogen at atmospheric pressure has been worked out and the constants in the formula—

$$\log r' = a + b \log r$$

determined.

It may be added in conclusion that though exceptional accuracy is not claimed for these results yet it is believed that they are fairly correct.

Admiralty Physical Laboratory,
South Kensington,

12th April, 1919.

UNIVERSITY OF TORONTO STUDIES

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